

UNPRECEDENTED QUARTZ/WATER INTERFACE STRUCTURE DETERMINED BY PHASE-SENSITIVE SUM FREQUENCY VIBRATIONAL SPECTROSCOPY

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RESEARCH OBJECTIVES

Natural chemical processes are initiated at interfaces between aqueous solutions and mineral surfaces. Over the past few years, large advances have been made in the elucidation of mineral surface structure in contact with water (e.g., Eng et al., 2000), and metal sorption topologies (Brown and Sturchio, 2002), but much less is understood about the organization of water on surfaces. Water acts to stabilize particular surface molecular geometries, solvate near-surface ions, and promote chemical reactions via proton and electron transfer—but details of these operations are poorly known on a molecular level. Our work seeks to determine water structure on a range of mineral surfaces as a function of pH, ionic strength, and complexation density (Ostroverkhov et al., 2004). We then intend to use this information to bootstrap molecular-dynamics (MD) simulations of interface phenomena, ultimately allowing modeling of interface reactions.

APPROACH

One of the most powerful tools for investigating interface water structure is sum frequency vibrational spectroscopy (SFVS). SFVS is a two-photon process in which tunable infrared (IR) light is mixed with green light at a mineral surface under solution. As a result of the broken symmetry at the interface, there is a small probability that light at the sum frequency of the two light beams will be generated. Studying this signal allows measurement of the vibrational spectrum only of interface species. SFVS has been used for studying air/liquid, solid/liquid, and other types of interfaces, but as usually employed, the method only detects the spectral amplitude. However, we have developed a method for obtaining SFVS spectra containing both amplitude and phase contributions. This is done by using a reference signal of known phase and allowing it to interfere with the SFVS signal from the interface. By doing this for two different phase reference signals, we can deduce the magnitude and both the real and imaginary parts of the SFVS spectrum. Because the imaginary part yields direct information on the orientation of water dipoles, we can obtain more information on interface water than ever previously measured (Figure 1).

ACCOMPLISHMENTS

By using the Phase-Sensitive (PS)-SFVS technique on quartz (0001) surfaces, we found: (1) that the lower-frequency IR band

usually attributed to “ice-like” tetrahedrally bonded water is actually composed of two contributions, and (2) that the “ice-like” water molecules orient themselves

quite differentially from interface “liquid water” in response to pH changes (Ostroverkhov et al., 2005). In particular, the “ice-like” water protons resist reorienting as pH is changed until a relatively large surface charge is produced, whereas the “water-like” protons shift positions readily at slight pH changes above the point of zero charge.

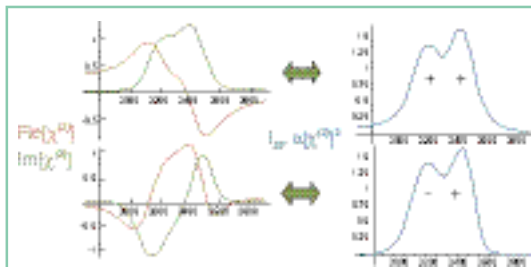


Figure 1. Right: simulated magnitude spectra of interface water having different dipole orientations for the low-frequency (“ice-like”) contribution. The spectra appear identical. Left: Decomposition into real and imaginary parts. The dipole orientation effects are clearly visible.

SIGNIFICANCE OF FINDINGS

Our results yield new information that can be precisely compared to MD simulations of interface water, and we

have already obtained good agreement using MD performed with the Center of Advanced Materials for Purification of Water with Systems, a National Science Foundation Science and Technology Center. This work should lead to a new level in molecular modeling of interface reactions.

RELATED PUBLICATIONS

- Brown, G.E., and N.C. Sturchio, An overview of synchrotron radiation Applications to low temperature geochemistry and environmental science. Reviews in Mineralogy and Geochemistry, 49, 1–115, 2002.
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- Ostroverkhov, V., G.A. Waychunas, and Y.R. Shen, New information on water interfacial structure revealed by phase sensitive surface spectroscopy. Phys Rev Letters, 94, 046102, 2005.
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ACKNOWLEDGMENTS

This project was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

